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Test Report for NG Sensors GTX-1000

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Abstract

This report describes initial testing of the NG Sensor GTX-1000 natural gas monitoring system. This testing showed that the retention time, peak area stability and heating value repeatability of the GTX-1000 were promising for natural gas measurements in the field or at the well head. The repeatability can be less than 0.25% for LHV and HHV for the Airgas standard tested in this report, which is very promising for a first generation prototype. Ultimately this system should be capable of 0.1% repeatability in heating value at significant size and power reductions compared with competing systems.

ACKNOWLEDGMENTS

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NOMENCLATURE

NG	Natural Gas
GC	Gas Chromatography
TCD	Thermal Conductivity Detector
DOE	Department of Energy
SNL	Sandia National Laboratories

1. INTRODUCTION

Testing of the NG Sensors Technology first generation GTX-1000 natural gas (NG) monitoring system (Figure 1) was conducted on December 3, 5 and 8 of 2014. Briefly, the prototype utilizes a sampling loop, gas chromatography (GC) columns and a thermal conductivity detector (TCD) for determining the components and heating value of NG mixtures in slightly less than 16 minutes. A cylinder of ultra-high purity helium is used as the GC carrier gas in this system, and GC temperature ramping is used to improve separation performance. The test conditions for this report are given in Table 1.

Figure 1: GTX-1000

Table 1: GC Apparatus and Test Conditions

Regulated Helium Head Pressure	25 psi
Sample Loop Volume	1 mL
Sample Loop Pressure and Temp.	630 Torr (atmospheric, unregulated), 50°C
First GC Specifications	1 m x 1/8" dia. Stainless steel Hayesep-D packed; fixed gas separation
First GC Temperature	40°C isothermal for 2 minutes; ramp 30°C/min to 250°C and hold
Second GC Specifications	30 m, 0.53mm dia. 5 micron DB-1 wall coated capillary
Second GC Temperature	Uncontrolled slightly super-ambient
TCD Temperature	150°C

The system was first calibrated using an Airgas NG standard (Cylinder S7804773) on December 3, 2014. GC peak areas in the calibration run were used to calculate the percentages of the

constituents found in subsequent performance testing. The mole percent concentration, C_x, of component x in a NG mixture was determined by the formula

$$C_x = \frac{A_x}{A_{cal(x)}} \cdot C_{cal(x)}$$

where A_x is the peak area of x in a given performance testing run. The calibration factors, $C_{cal(x)}$, for a given component x are provided in **Table 2**.

Table 2: Manufacturer's Certification for AirGas Cylinder S7804773.

Components (x) of AirGas S7804773	**Certified Concentration, C_{cal} (mol%)**
Hexane	0.0314
Iso-Pentane	0.1004
N-Pentane	0.1008
Neo-Pentane	0.1013
Iso-Butane	0.299
N-Butane	0.2963
Carbon Dioxide	1.01
Propane	1.01
Nitrogen	2.49
Ethane	5.03
Methane	89.5308
Total	100

2. PEAK AREA AND RETENTION TIME STABILITY TESTING WITH THE AIRGAS STANDARD

Five repetitions with the Airgas NG Standard (cylinder S7804773**)** were performed to quantify the repeatability of the measurement. The coefficient of variance (the ratio of the standard deviation to the mean) of the raw peak areas for the various components of the mixture are provided in Figure 2. Comparing the two plots, the carbon dioxide concentration in the first repetition was deemed to be an outlier. Removing the data from the analysis, and plotting the results in the bottom of Figure 2, one can see that for the most part the variance in individual peak areas was less than 4%, with the largest variance in the second labeled hexane peak. For the high concentration components, C1-C4, the peak area variance for the GTX-1000 is less than 1%, which is very important for heating value repeatability.

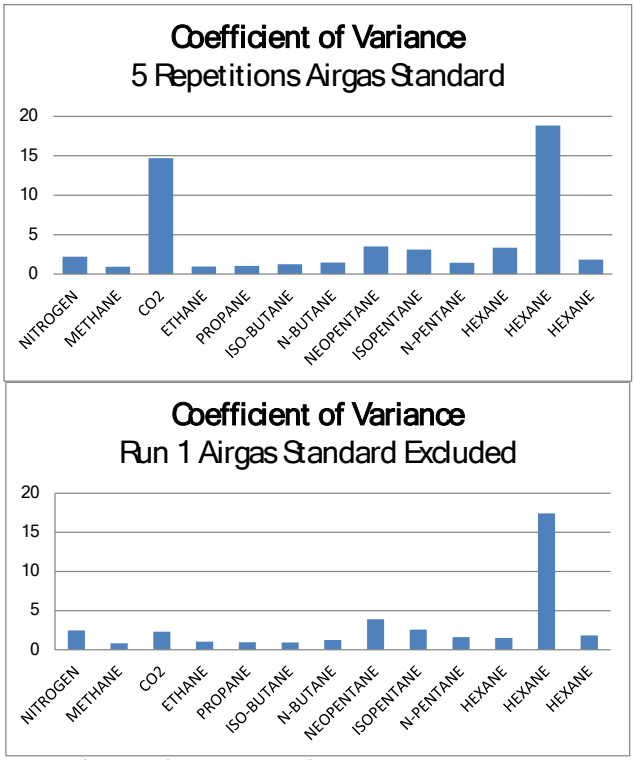

Figure 2: Coefficient of variance (in percent) in peak areas (raw data) for the components of the Airgas NG standard S7804773.

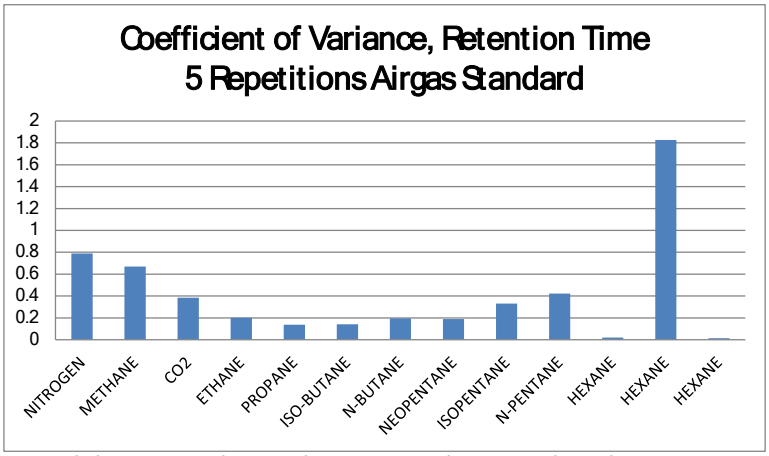

Figure 3: Coefficient of variance (in percent) in retention time (raw data) for the components of the Airgas NG standard S7804773.

The retention time variance for the Airgas cylinder data is plotted in Figure 3. The variance in the retention time for the GTX-1000 for all gas components is less significantly less than 1%, indicating stable performance. Furthermore, the peaks are well separated in time and are clearly identified in the software based on calibrations. This speaks well of the stability of the chromatography in the GTX-1000. The main retention time outlier is the second apparent hexane peak. The latter is related to an issue discussed below, which should be soluble by simple engineering modifications to the system.

3. PEAK AREA AND RETENTION TIME STABILITY TESTING WITH THE SCOTTY STANDARD

Having performed calibrations and stability testing with the Airgas standard, studies with a different standard, Scotty NG standard 303102, were performed next. The composition of this standard is shown in Table 3. Comparing with Table 2, the composition of this standard is seen to be quite different in than the Airgas standard. Among other things, this standard contains no hexane, though two to three peaks appear in the same retention time window and with roughly the same peak area as the peaks identified as hexane in the Airgas standard.

Table 3: Manufacturer's Certification for the Scotty 303102 NG standard.

Components (x) of Scotty 303102	**Certified Concentration, C_{cal} (mol%)**
Hexane	0
Iso-Pentane	0.506
N-Pentane	0.51
Neo-Pentane	0
Iso-Butane	3.01
N-Butane	3
Carbon Dioxide	0.506
Propane	7
Nitrogen	9
Ethane	12.5
Methane	69.968
Total	100

The coefficient of variance in peak area for the Scotty 303102 standard is slightly worse than the Airgas standard, but we have reason to believe that this standard may have been varying, as described below. The retention time stability for the Scotty 303102 Standard, like the Airgas standard, is excellent (Figure 5).

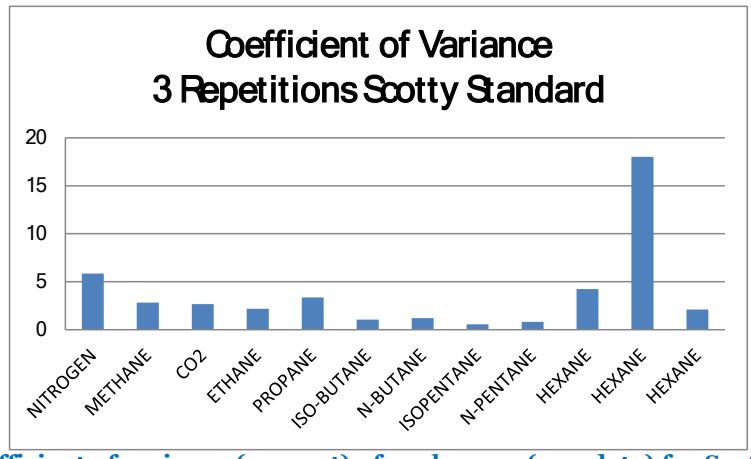

Figure 4: Coefficient of variance (percent) of peak areas (raw data) for Scotty 303102 NG Standard.

The appearance of two to three apparent hexane peaks is the largest issue we find with this data. There is no hexane in the Scotty standard according to the certification, yet apparent hexane peaks appear at nearly the same retention times and at nearly the same concentrations as in the Airgas standard. At this moment, we believe this error is most likely caused by the low temperature of the sample valve (50°) and lack of temperature control of the DB-1 GC. The implementation of a back flush step at about 14 minutes is also implicated in this issue. As seen in Figure 5, the retention time variance of the first and third apparent hexane peaks is exceptionally low by comparison with most other peaks. This could indicate that these peaks are due to pressure variations due to valve state switching, which are performed at well-defined times. Meanwhile, the variance in the second apparent hexane peak area and retention time is the highest of any of the peaks. It is possible that this peak is actually hexane carrying over from the Airgas experiments to the Scotty standard testing through condensation in the sample loop or unheated GC; thus the suggestion for temperature control of these components. This would be considered best practice for field NG analyses anyhow. But, the fact that the perceived hexane peak area in successive tests with the Scotty standard does not diminish relative to the Airgas standard, suggests again that the problem may be more related to pressure variations produced by back flush valve switching.

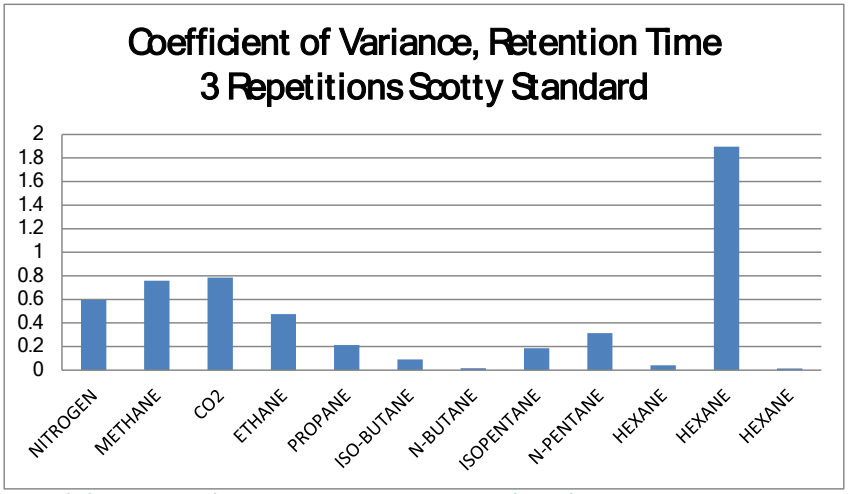

Figure 5: Coefficient of variance (percent) of retention time for Scotty 303102 Standard.

4. HEATING VALUE REPEATABILITY

The low concentration of the hexane in these two standards, 0.03 and 0 mol %, respectively, means that the absolute error in heating value due to the problems with hexane mentioned above, are minor. Theoretically, the maximum error in lower heating value (LHV) and higher heating value (HHV) are 1.38 and 1.49%, respectively, for the Airgas standard due to a misreading in hexane. The hexane peak issues can be solved by engineering modifications, as discussed in the recommendations below. Once that issue is resolved, the absolute accuracy of the heating values can be determined. For the moment, however, the repeatability of the heating value can be reported.

The run-by-run repeatability of the GTX-1000 unit for the Airgas standard is reported in The data shows that the repeatability in LHV and HHV for all runs is less than 1.5%. However the second repetition heating value is more than one standard deviation away from the mean meaning it could be considered an outlier. The repeatability is then less than 0.25% for LHV and HHV for this standard, which is promising for a first generation prototype. We should also note that the peak area calibration was performed on December 3 and testing on December 5 and 8. With peak calibrations closer to testing, performance should further improve.

Table 4. Standard published heating values for the various components of the mixture were used to calculate the heating values for each of the components in each of the runs based on their concentrations, as reported by the GTX-1000 software. The total heating value for a given run was calculated as the sum of the component heating values. The percent difference in heating value was calculated as

$$100 \cdot |HV_n - HV_{n+1}|/HV_n$$

Here, HV_n is the heating value for run n, and HV_{n+1} is the heating value for the successive run. The data shows that the repeatability in LHV and HHV for all runs is less than 1.5%. However the second repetition heating value is more than one standard deviation away from the mean meaning it could be considered an outlier. The repeatability is then less than 0.25% for LHV and HHV for this standard, which is promising for a first generation prototype. We should also note that the peak area calibration was performed on December 3 and testing on December 5 and 8. With peak calibrations closer to testing, performance should further improve.

Table 4: Run-to-Run Heating Value Repeatability with the Airgas Standard. Percent error in LHV and HHV comparing successive repetitions is indicated.

Repeat	LHV	HHV
1	0.28	0.27
2	1.44	1.44
3	0.24	0.24
4	0.21	0.20

Average (All)	0.54	0.54
Standard Dev. (All)	0.60	0.60
Coefficient of Variance (All)	111.20	111.72
Average (1, 3, 4)	0.24	0.24
Standard Dev. (1, 3, 4)	0.04	0.03
Coefficient of Variance (1, 3, 4)	14.56	13.72

The run-by-run repeatability using the Scotty standard is given in Table 5. This data is included for completeness, with the caveat that a large amount of error is suspected from this standard itself in terms of actual composition. From the chromatograms, it is noted that iso-pentane is not produced in the last two repetitions, while n-pentane also was absent from the last run. This fact, and the fact that the peak area variability for this standard (Figure 4) was substantially greater than for the Airgas standard (Figure 2) could indicate that the Scotty calibration standard was out of date and drifting in time. Nonetheless, this data shows that it is possible to achieve less than 0.5% run-to-run variation in heating value for this standard using the GTX-1000.

Table 5: Run-to-Run Heating Value Repeatability with the Scotty Standard. Percent error in LHV and HHV comparing successive repetitions is indicated. See cautionary notes in the text on this standard.

Repeat	LHV	HHV
1	0.15	0.15
2	4.24	4.24
3	1.43	1.46
4	0.40	0.37
Average (All)	1.55	1.56
Standard Dev. (All)	1.87	1.88
Coefficient of Variance (All)	120.49	120.85
Average (1, 3, 4)	0.66	0.66
Standard Dev. (1, 3, 4)	0.68	0.70
Coefficient of Variance (1, 3, 4)	102.55	105.99

5. RECOMMENDATIONS

Based on these results we have several recommendations. In terms of engineering modifications to improve response for hexane (and higher order constituents), we recommend temperature controlling the valve and DB-1 column to greater temperatures than what are currently being used. Eliminating the back flush step, or changing the timing of this step if it is deemed necessary, should also be considered.

In order to understand the effect of the latter on the appearance of hexane peaks, we recommend two types of testing. First, air (blank) injections could be performed to see if apparent hexane peaks still occur. Second, modify the back flush valve timing to see if the apparent hexane peaks shift accordingly. Either of these tests might help identify the source of the apparent hexane peaks.

For ultimate chain of custody use, NG Sensors might also consider including a pressure transducer at the sample inlet, and performing a calibration run using an onboard standard immediately prior to each field test.

Given the potential issues mentioned concerning the Scotty standard in this report, we recommend another set of experiments in which testing is performed with a new set of certified gas standards. This testing could with the existing GTX-1000, or a modified version which corrects the noted issues with hexane.

6. SUMMARY

This testing showed that the retention time, peak area stability and heating value repeatability of the GTX-1000 were promising for natural gas measurements in the field or at the well head. The repeatability can be less than 0.25% for LHV and HHV for the Airgas standard tested in this report, which is very promising for a first generation prototype. Ultimately this system should be capable of 0.1% repeatability in heating value at significant size and power reductions compared with competing systems. We encourage further development and testing of this platform.

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